



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 307 139 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: 06.04.94 (51) Int. Cl. 5: C08F 283/01, C08F 299/04,
C08J 9/00
(21) Application number: 88308121.8
(22) Date of filing: 01.09.88

(54) Vesiculated polymer granules.

- (30) Priority: 08.09.87 US 95419
(43) Date of publication of application:
15.03.89 Bulletin 89/11
(45) Publication of the grant of the patent:
06.04.94 Bulletin 94/14
(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE
(56) References cited:
EP-A- 0 083 188
FR-A- 2 074 188
FR-A- 2 206 346

- (73) Proprietor: C-I-L Inc.
90 Sheppard Avenue East
North York Ontario M2N 6H2(CA)
(72) Inventor: Hayes, Peter Charles
2500 Keele Street
Apartment 304
Toronto Ontario, M6L 2N5(CA)
Inventor: Ferguson, Loreen Doris
1547 Mississauga Valley Boulevard
Apartment 2101
Mississauga Ontario, L5A 3X8(CA)
Inventor: Macas, Tadas Stepas
782-11th Street
West Vancouver British Columbia, V7T
2L9(CA)

- (74) Representative: Gore, Peter Manson et al
W.P. THOMPSON & CO.
Coopers Building
Church Street
Liverpool L1 3AB (GB)

EP 0 307 139 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to vesiculated polymer granules, aqueous compositions comprising said granules and to said compositions comprising said granules and fibrous material of use in papermaking.

5 Paper is typically made from aqueous suspensions of fibrous cellulosic or non-cellulosic material which may have been delignified and/or bleached, e.g. plant matter, such as trees, cotton, bagasse, and synthetic polymers, such as rayon. To the aqueous fibrous suspension are generally added sizing materials, wet and dry strength additives, defoamers, biocides, dyes, and particularly, retention aids and fillers. The suspension (furnish) is transferred to a forming wire for water drainage to concentrate solids, and subsequently dried to
10 the desired basis weight.

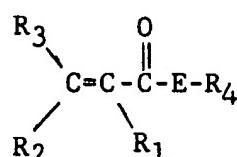
The development of fibrous systems having a high opacity has always been a concern to paper manufacturers. The degree of opacity of a particular substrate is the result of diffuse light-scattering which occurs when visible radiation is reflected from particles on the surface of the substrate and in the substrate medium itself. It has been customary to use high density inorganic mineral fillers, such as calcium
15 carbonate and certain clays, to enhance the opacity of paper sheets. Unfortunately, the use of such fillers has several disadvantages in the manufacture of paper. Most inorganic mineral fillers possess a low opacity-to-weight ratio when included in paper. In addition, the generally low retention of the inorganic mineral opacifiers in the paper results in a financial loss by virtue of the by-product waste produced from the wire during sheet formation. More importantly, this poor filler retention may result in contamination of
20 streams, lakes and other waterways.

It is customary to incorporate in the dilute paper furnish, just before formation on the wire, small amounts of polyelectrolyte retention aids to give improved retention of the fibrous material, fillers and fines on the wire during sheet formation. This reduces, somewhat, the loss of the filler to the by-product waste.

It has been suggested that microencapsulated polymers can be incorporated in a paper sheet to
25 enhance opacity. The substantially spherical polymers can be added in the dilute paper furnish before formation on the wire as substitutes for inorganic mineral fillers. These microcapsular opacifiers can also be incorporated in coatings for fibrous or non-fibrous substrates. For example, Canadian Patent No.856,861 describes polymer granules with a vesiculated structure that can be utilized in a coating composition and polymer films to impart an opacity which is greater than non-vesiculated granules of the same composition.

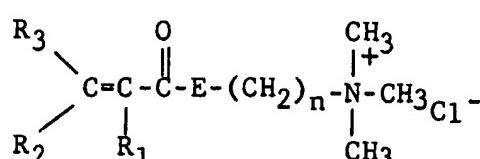
30 It has now been found possible to provide a means for increasing the retention of pigmented and/or non-pigmented vesiculated granules in a paper sheet. It has also been found possible to provide a reduction in the amount of opacifier which is lost during the formation of paper on the forming wire.

According to the present invention there are provided vesiculated granules of cross-linked carboxylated polyester resin prepared by the free radical polymerization of a dispersion comprising (a) a substantially
35 water-insoluble ethylenically unsaturated monomer; (b) a carboxylated unsaturated polyester resin having an acid value of from 5 to 50 mg KOH/g; (c) water; (d) a base; and (e) up to 30 weight percent, of the non-volatile portion of both the polyester resin and the acryloyl derivative, of a polymerizable alkyl acryloyl derivative of the formula:



wherein R₁, R₂ and R₃ are selected from H and CH₃; E is NH or O; R₄ is C₁₋₆ alkyl substituted with Z; wherein Z is NR₅R₆; wherein R₅ is C₁₋₄ alkyl and R₆ is H; or R₅ and R₆ are independently C₁₋₃ alkyl; and quaternary C₁₋₃ alkyl salts thereof.

50 Preferably, the alkyl acryloyl derivative has the general formula:



wherein R₁, R₂ R₃ and E are as hereinbefore defined and n is selected from 1 to 3.

The vesiculated beads provided herein have a highly cross-linked polymeric body constituted by a carboxyl-functional unsaturated polyester resin cross-linked with an ethylenically unsaturated monomer and an alkyl acryloyl derivative copolymerized therewith.

We have found in accordance with the present invention that the chemical incorporation of an alkyl acryloyl derivative electrolyte within a pigmented or non-pigmented vesiculated granule to constitute a polyelectrolyte retention aid provides enhanced retention of said granule, filler and fines within a fibrous cellulosic or non-fibrous cellulosic paper sheet. Surprisingly, it has been found that when these pigmented and/or non-pigmented vesiculated granules are added to an aqueous paper pulp furnish before being formed into a paper sheet on the forming wire, the resulting paper sheet achieves an enhanced opacity.

Thus, in a further feature the invention provides an aqueous composition comprising vesiculated granules according to the invention as hereinbefore defined and a fibrous cellulosic or non-fibrous cellulosic material in the form of a paper pulp.

In a further feature of the invention, the vesicles contain particulate solids. The particulate solids may be dispersed in a liquid in which the polymer is insoluble or may be associated with substantially gaseous components alone. For example, the particulate solids used in the granules may be any suitable organic or inorganic filler. Such fillers include those finely divided materials which have been conveniently employed for the purpose of enhancing optical properties, such as, for example, opacity in a paper sheet. Suitable fillers include, for example, TiO₂, CaCO₃, Al₂O₃.3H₂O, barytes (BaSO₄), clay, CaSO₄, CaSiO₃, talc, and the like. Preferred inorganic fillers for the purpose of the present invention are TiO₂, CaCO₃, Al₂O₃.3H₂O, BaSO₄, and clay, with titanium dioxide being particularly preferred.

Any desired filler particle size may be used, as long as it is suitable for incorporation into the vesicular structure. Thus, for example, titanium dioxide having a mean particle size between 1x10⁻⁴ and 3.5x10⁻⁴ mm (between 0.1 and 0.35 microns) is highly suitable for the purposes of this invention.

The technique of preparing porous granules from carboxylated, unsaturated polyester resin by emulsifying water into the polyester resin in the presence of a base and then polymerizing the resin has been known for some time. The background to the subject is well covered in the literature, for example, in articles by Kershaw (Australian OCCA Proceedings and News, 8 No. 8, 4 (1971)), and Treier (TAPPI, 55 No. 5, (1972)). Numerous patents relating to these granules have also been issued, which include United States Patent No.'s 3,822,224; 3,879,314; 3,891,577; 3,933,579; 4,089,819; 4,321,332; and particularly, Canadian Patent No. 1,139,048. Although it is not intended to limit the present invention to any particular process of manufacture or choice of carboxylated, unsaturated polyester resins of which the vesiculated beads are comprised, the process of preparation of vesiculated polyester resin granules as outlined in Canadian Patent No. 1,139,048 is preferred. However, in the preparation of prior art vesiculated granules it is known that a thickening agent is required to stabilize the granules after formation by the "double emulsion" process. In the absence of the thickener, or constant agitation, the granules will settle into a hard-packed layer at the bottom of the container. This tendency to settle or aggregate is undesirable in that "grit" particles may form, and the settled layer is difficult to resuspend. A further disadvantage is the requirement of additional amine to the system to activate the thickener, which contributes to an undesirable odour.

Surprisingly, we have now found that it is possible to prepare dimensionally stable granules by a double emulsion process from which all the suspending thickener and associated amine can be eliminated.

Accordingly, in a further aspect the invention provides an aqueous composition comprising vesiculated granules as hereinbefore defined.

Carboxylated unsaturated polyesters which will cross-link by reaction with ethylenically unsaturated monomers are well known. Suitable polyester resins are usually the condensation products of dicarboxylic acids (or their corresponding anhydrides) and dihydric alcohols, polymerizable unsaturation being introduced into the chain by the use of a proportion of α,β -ethylenically unsaturated acid. The polyester resins from which selection can be made are condensation products of polybasic acids (or their corresponding anhydrides) and dihydric alcohols. Polymerizable unsaturation can be introduced into the molecule by the selection of a α,β -ethylenically unsaturated acid, optionally in combination with a saturated acid or anhydride.

Thus suitable acids include, for example, unsaturated aliphatic acids, e.g. maleic, fumaric and itaconic acids; saturated aliphatic acids, e.g. malonic, succinic, glutaric, adipic, pimelic, and azelaic.

Suitable dihydric alcohols include, for example, ethylene glycol, poly(ethylene glycols) e.g. diethylene glycol, hexane 1,6-diol, propylene glycol, di-cyclohexanol and neopentyl glycol. Alternatively, the alcohol may be one which initially contained three or more hydroxyl groups, the groups in excess of two optionally being at least in part etherified with, for example, a monohydric alcohol e.g. methanol, ethanol and n-butanol or esterified with monobasic acid, e.g. benzoic acid, p-tertiary-butyl benzoic acid and chain like aliphatic

acids of up to 18 carbon atom chain length e.g. coconut oil monoglyceride.

The methods by which unsaturated polyesters of this type are formulated and made are well known in the art. The resins preferred for this invention are formulated with a glycol excess. The glycol excess determines the final viscosity.

5 It is necessary in the working of the present invention that the acid value of the polyester lie within certain limits. We have found it necessary to select polyesters whose acid values lie in the range 5 to 50 mg KOH/g, preferably 10 to 25 mg KOH/g and most preferably 15-20 mg KOH/g. Acid values greater than 23 may result in low opacity beads when used in coatings. If the acid values are much less than 15, instability may occur during the curing stage. This results in the formation of bead aggregates and in the 10 extreme case, complete aggregation of the batch can occur.

The unsaturated monomer in which the unsaturated polyester resin is dissolved and cross-linked must be substantially water-insoluble. Monomers which have a solubility at 20 °C of less than 5% (w/w) in water are considered to be suitably water-insoluble for the present purpose. A single monomer or a mixture of monomers may be used and in general the monomer will contain only a single polymerizable double bond.

15 However, it is known that polyfunctional monomers, that is, monomers containing more than one polymerizable double bond, may also be used to cross-link unsaturated polyester resins. Such polyfunctional monomers are, however, normally present only as a minor constituent of a mixture of monomers, the major proportion of which is monofunctional monomer. Hence mixtures comprising e.g. divinyl benzene may be used in the performance of the present invention.

20 The preferred ethylenically unsaturated monomers are selected from styrene, the mixed isomers of methyl styrene commercially available as 'vinyl toluene' and methyl methacrylate, because of the ease with which they can be copolymerised with the unsaturated resin. For best results, it is preferred that the monomer comprises at least 50% by weight of styrene.

25 The choice of monomers is not, however, restricted to the above monomers alone. Bearing in mind the requirements that the total monomer must be substantially insoluble in water and also be a solvent for the unsaturated polyester resin, there may be present in a minor proportion other polymerizable unsaturated monomers to, for example, modify the physical properties of the coreacted resins. Typical co-monomers are, for example, ethyl acrylate, n-butyl methacrylate, and acrylonitrile.

30 The alkyl acryloyl derivative which is dispersed within the unsaturated polyester resin and unsaturated monomer must be substantially water soluble, or can be made water soluble through the formation of a quaternized structure or by other methods known in the art. A single acryloyl derivative or a mixture of acryloyl derivatives may be used and in general the acryloyl root structure will contain only a single polymerizable double bond. In some cases the acryloyl root structure may contain two or more polymerizable double bonds.

35 Typical examples include MAPTAC (methacrylamidopropyltrimethylammonium chloride), TMAEMC (2-trimethylammoniummethylmethacrylic chloride), DANA (3-dimethylaminoneopentylacrylate) and BAEMA (2-t-butylaminoethylmethacrylate)

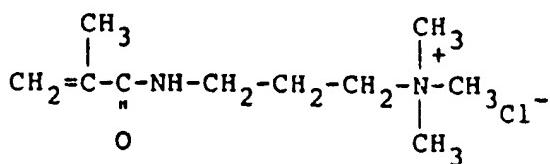
40

45

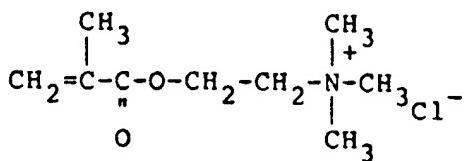
50

55

MAPTAC

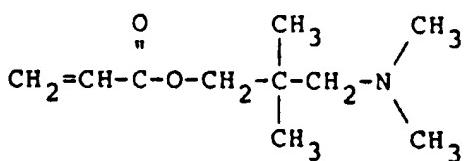


TMAEMC



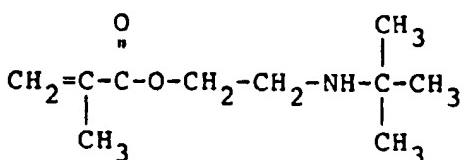
15

DANA



25

BAEMA



30

In general, we have found that the upper limit of usefulness of such acryloyl derivatives is up to 30 weight percent of the ethylenically unsaturated polyester, preferably 20 weight percent, and more preferably 15 weight percent based on the non-volatile portion of both the polyester resin and the acryloyl derivatives.

Higher concentrations of the acryloyl derivative quaternized structure, for example, may give a destabilising effect to the emulsion.

40 Optionally a few percent by weight of a non-polymerizing organic liquid, e.g. *n*-butanol or toluene, may be mixed with the monomer to increase the solubility of the polyester resin therein or may be introduced as an incidental part of the process, e.g. in preparing the polyester.

45 It is highly preferred that there be included in the dispersions used in this invention a surfactant chosen from those which are well known in the art. Typical examples of suitable species are the sulphates of nonylphenol and dodecylphenol ethoxylates wherein the alkylene oxide chain comprises at least 5 ethylene oxide units. The surfactant is typically present to the extent from 0.75 - 7.5% (preferably 3.0 - 4.5%) by weight of dispersant solids per volume of total granule solids and may be added initially to any of the phases of the dispersion prior to polymerization.

50 The base used in this invention may be selected from the polyamine bases of the variety described by Gunning in United States Patent No.'s 3,879,314 and 3,923,704 or the metal oxide, hydroxide and salt bases described by Beresford in United States Patent No. 4,321,322. We have found the preferred base is magnesium oxide. When an amine base is used, sufficient amine should be present such that there are present from 0.3 - 4.0, preferably 1.3 - 3.2 amine groups per polyester carboxyl group. When a metal oxide, hydroxide or salt base is used, sufficient base should be present such that there is present from 0.8 - 1.8 equivalents of metal cation per equivalent of polyester carboxyl group.

55 Particulate solids, as hereinbefore described, may be optionally included in the dispersions according to the present invention.

The particulate fillers may be dispersed in the polyester solution prior to the emulsification of water therein, or into the water to be emulsified therein or into both, the incorporation into the water being an especially convenient method. The incorporation of the filler or fillers may be carried out using methods and

dispersing agents known to the art. A further method of imparting pigmentation is the addition of base in excess of the quantity needed for complete neutralization of the carboxyl groups of the polyester resin. All of the bases preferred in the present invention are capable of acting as extender pigments and some of them, for example, zinc oxide, are primary opacifying pigments in their own right. Thus, the addition of a quantity of base in excess of that required for complete neutralization of the carboxyl groups for the purpose of pigmentation is encompassed by the present invention.

Unusual effects may be produced in a material comprising granules in which the filler is at least in part coloured. For example, the filler may comprise iron oxide, phthalocyanine, quinacridone or the like. Chemical or physical tagging agents may be included in the vesicles or in the dispersion stage, included are dyes, ultra-violet absorbers, quenchers, or brighteners, fluorescent materials and like additives.

Preferably, the particulate solids concentration is no more than 60% by volume of the vesicle. While the size of the chosen particles depends on the actual vesicle diameter, it is preferred that the maximum particle diameter should be 0.01 mm (10 microns).

The preferred method of preparation of granules is the "double emulsion" method referred to hereinabove. The initial stage in the preparation of the novel polymeric vesiculated granules is the emulsification of water into the solution in ethylenically unsaturated monomer or carboxylated unsaturated polyester resin (the solution in ethylenically unsaturated monomer or carboxylated unsaturated polyester resin shall hereinafter be referred to as "the polyester solution" and the emulsion of water in the polyester solution shall hereinafter be referred to as the "first emulsion"). The alkyl acryloyl derivative may be added to the polyester solution or to the water in the first phase with mechanical agitation. The amount of the alkyl acryloyl derivative added to the polyester resin solution is a portion of the total amount desired such that when the remaining portion is added to the second emulsion stage the stable double emulsion of system is maintained. Preferably, the alkyl acryloyl derivative should be added in the ratio of from 0 : 100 to 55 : 45, first emulsion : second emulsion on a weight basis. The mechanical agitation is continued until the viscosity of the emulsion is substantially constant.

The agitation is carried out in the presence of the base which may be present in the polyester solution, the water or both. If pigmented granules are required, the pigment may be added at this stage, or it may be added to the water, the polyester solution or both prior to the formation of the first emulsion.

The first emulsion is dispersed in water which contains the second portion of the alkyl acryloyl derivative and a stabilizer for the dispersed first emulsion particles and stirred until the desired granule size is achieved; this is the "double emulsion". The stabilizer may be chosen from the wide range of materials known to be suitable for this purpose but we have found that an especially suitable material is a water-soluble partially hydrolysed poly(vinyl alcohol) with a degree of hydrolysis of 86 to 89% and a viscosity of 44-50 mPa s (centipoise) (30 °C 4% wt. solution, BL type viscometer). A concentration of stabiliser of the order of 0.1 - 2.0 % by weight of the total water (vesicular water and continuous phase water) gives satisfactory results.

The surfactant may be added at any stage of the process prior to polymerization and to any phase of the double emulsion.

Polymerization of the polyester resin is effected by free radical means. This can be achieved by the use of a free radical initiator such as an organic peroxide or by exposure to a radiation source such as ultraviolet radiation or a radioactive element. When a free radical initiator is used it may be conveniently dissolved in the polyester resin solution before the dispersion of the solution in water or it may be added to the continuous water phase following the formation of the double emulsion.

The preferred initiation system is a redox system of diethylene triamine and cumene hydroperoxide triggered by ferrous ions derived from ferrous sulphate. These three materials are added in the following sequential order to the continuous phase: ferrous sulphate, diethylene triamine, and cumene hydroperoxide.

With the incorporation of the alkyl acryloyl derivatives in the first and second emulsion stages the vesiculated polyester granules thus formed have excellent colloidal stability and anti-settling properties. The shelf storage life of the emulsion is extended beyond that reasonably expected for granules prepared without the acryloyl derivatives. The aqueous slurry of vesiculated polyester granules thus formed may be used directly in an aqueous paint formulation, or in paper coatings, or paper wet-end applications. The aqueous slurry of vesiculated polyester granules may be dewatered, by any convenient means, for example by the method described in United States Patent No. 4,154,923 and subsequently redispersed in an aqueous or non-aqueous medium, or incorporated into a paste, for example, for use as a filler or a putty, or in a polymer film.

The paper compositions prepared using granules as hereinbefore defined have consistently improved first-pass retention.

The papermaking process can be carried out using a conventional furnish formed in part or totally from hardwood, softwood and recycled pulps and/or broke if desired incorporating an internal sizing agent, for example, natural and fortified rosins or an aqueous ketene dimer emulsion.

5 The aqueous compositions of use in accordance with this invention can be employed in alkaline papermaking system, that is systems in which the paper furnish is maintained at a neutral or alkaline pH value, or in an acid papermaking system, that is systems in which the paper furnish is maintained at an acid pH value.

In yet a further feature the invention provides paper containing dispersed therein vesiculated polymer granules as hereinbefore defined.

10 The invention is further described with reference by way of example only to the following examples in which all parts are expressed by weight.

EXAMPLE 1

15 This example illustrates the preparation of 0.01 mm (10 microns) pigmented vesiculated polyester resin granules in which the alkylacryloyl derivative is in the first and second emulsion stages. In this example the alkyl acryloyl derivative was MAPTAC.

20

25

30

35

40

45

50

55

	<u>GROUP</u>	<u>MATERIAL</u>	<u>PARTS (W/W)</u>	
5	A	water	3.089	
		dispersant	(1)	0.237
		antifoam	(2)	0.014
	B	titanium dioxide pigment	(3)	9.250
10	C	MAPTAC	(4)	0.237
	D	water		4.267
15	E	water		1.292
	F	polyester	(5)	7.592
		styrene	(6)	4.211
		magnesium oxide	(7)	0.042
20	G	hydroxyethyl cellulose	(8)	7.538
		poly(vinyl alcohol)	(9)	4.377
		MAPTAC		0.984
		water		28.628
25	H	water		25.701
	I	ferrous sulphate	(10)	0.003
		diethylene triamine	(11)	0.041
30	J	cumene hydroperoxide	(12)	0.080
	K	bactericide	(13)	0.073
		ammonia solution	(14)	0.165
		water		<u>2.179</u>
35				100.000

- (1) Dispersant: a 60% wt. solids ammonium
40 nonylphenoxyethoxy sulphate in ethanol.
Fenopon* CO-436 (ex. GAF Corp)
- (2) Antifoam: mineral oil and surfactant blend.
45 Proprietary Foamaster* NS1 (ex. Diamond Shamrock)
- (3) Titanium dioxide pigment: rutile grade with
50 organic surface treatment on an alumina based

inorganic coating. Tioxide* RHD6-X (ex. Tioxide)

- (4) MAPTAC: a 50% weight solids solution in water
5 Mhoromer* BM-613 (ex. Rohm Tech.)
- (5) Polyester: a 65% wt. solids solution of a
10 4.216/2.566/1.000 (molar) propylene glycol/maleic
anhydride/phthalic anhydride solution in styrene
- 15 (6) Styrene: commercially available material
(ex. Dow Chemical)
- 20 (7) Magnesium oxide: commercially available light
grade (ex. BDH Chemicals)
- 25 (8) Hydroxyethyl cellulose: a 1.5% wt. solids aqueous
solution of hydroxyethyl cellulose.
Natrosol* 250HR (ex. Hercules)
specification: i) viscosity = 1500-2500 mPa s (1500-2500 cp.)
30 Brookfield at 25°C using 1% wt. solution
ii) molar substitution for
ethyl = 2.5
- 35 (9) Poly(vinyl alcohol): a commercially available
7.5% wt. solids aqueous solution of poly(vinyl
alcohol) BP-24 (ex. Chang Chun Petrochemical Co.
40 Ltd., Taipei, Taiwan)
specification: i) degree of hydrolysis = 86-89%
ii) viscosity = 40-50 mPa s (40-50 centipoise)
45 BL type viscometer at 30°C using a 4% wt. solution
- (10) Ferrous sulphate: commercially available material
(ex. J.T. Baker Chemical Co.)
50 specification: hepta hydrate

(11) Diethylene triamine: commercially available material (ex. Union Carbide)

5

(12) Cumene hydroperoxide: a commercially available 78% active material (ex. Pennwalt)

10

(13) Bactericide: a commercially available 20% wt. active aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one. Proxel^{*} GXL
15 (ex. Imperial Chemical Industries PLC)

15

(14) Ammonia: a commercially available 30% wt. solution ammonium hydroxide in water. (ex. Stanchem)

20

* = trade mark

25

The pigmented vesiculated polyester resin granules were made as follows:

Materials "A" were mixed and pigment "B" added to "A" at a uniform rate while stirring. Stirring was increased to a high speed and continued until the pigment was completely dispersed. Material "C" was added while stirring, the water "D" was added to give a millbase.

30

Materials "F" were mixed until the magnesium oxide was completely dispersed. The millbase was washed into "F" using water "E". This was mixed with high speed stirring until the dispersed particles of the millbase were at least 0.001 mm (one micron) in diameter. This is referred to as the "first emulsion".

35

Materials "G" were blended together and the temperature adjusted such that when the first emulsion was added to materials "G" the resulting temperature was 25°C. The attention to the final temperature was found to be critical. The first emulsion was added to the temperature adjusted materials "G". The stirring was maintained at high speed until the droplets of the first emulsion were substantially 0.01mm (ten microns) or less in diameter. This is referred to as the "second emulsion".

40

The speed of the mixer was dropped to a slow stir. The "H" stage water temperature was adjusted such that the resulting temperature, when added to the double emulsion, would attain 35°C. The "H" stage water was added to the double emulsion.

Materials "I" were added to the second emulsion. The ferrous sulphate was first dissolved into a small amount of hot water before addition.

Material "J" was added, then the mixer was turned off. This was left undisturbed for a minimum of three hours to effect curing.

45

Materials "K" were added after curing using moderate stirring speed.

EXAMPLE 2

This example illustrates the preparation of 0.01 mm (10 microns) pigmented vesiculated polyester resin granules in which the alkyl acryloyl derivative is in the second emulsion stage only. For the purposes of this example the alkyl acryloyl derivative was chosen to be TMAEMC. The materials were as described in Example 1 except as noted.

55

EP 0 307 139 B1

GROUP	MATERIAL	PARTS (W/W)
A	water dispersant antifoam	3.089 0.237 0.014
B	titanium dioxide pigment	9.250
C	water	4.267
D	water	1.292
E	polyester styrene magnesium oxide	7.592 4.211 0.042
F	hydroxyethyl cellulose poly(vinyl alcohol) TMAEMC (15) water	7.538 4.377 0.763 28.628
G	water	26.159
H	ferrous sulphate diethylene triamine	0.003 0.041
I	cumene hydroperoxide	0.080
J	bactericide ammonia solution water	0.073 0.165 2.179
		100.000

(15) TMAEMC: an 80% wt. solids solution in water Mhoromer* BM-604 (ex.
Rohm Tech.)

* = Trade Mark

The pigmented vesiculated polyester granules were made as follows:

Materials "A" were mixed and pigment "B" added to "A" at a uniform rate while stirring. Stirring was increased to a high speed and continued until the pigment was completely dispersed. The water "C" was added to give a millbase.

Materials "E" were mixed until the magnesium oxide was completely dispersed. The millbase was washed into "E" using water "D". This was mixed with high speed stirring until the dispersed particles of the millbase were at least 0.001 mm (one micron) in diameter. This is referred to as the "first emulsion".

Materials "F" were blended together and the temperature adjusted such that when the first emulsion was added to materials "F" the resulting temperature was 25 °C. The attention to the final temperature was found to be critical. The first emulsion was added to the temperature adjusted materials "F". The stirring was maintained at high speed until the droplets of the first emulsion were essentially 0.01mm (ten microns) or less in diameter. This is referred to as the "second emulsion".

The speed of the mixer was dropped to a slow stir. The "G" stage water temperature was adjusted such that the resulting temperature, when added to the double emulsion, would attain 35 °C. The "G" stage water was added to the double emulsion.

Materials "H" were added to the second emulsion. The ferrous sulphate was first dissolved into a small amount of hot water before addition.

Material "I" was added, then the mixer was turned off, and the emulsion was left undisturbed for a minimum of three hours to effect curing.

Materials "J" were added after curing using moderate stirring.

Table A outlines some of the physical parameters obtained when pigmented vesiculated granules are prepared in accordance with the aforementioned methods of preparation for 0.01mm (10 micron) diameter granules.

EP 0 307 139 B1

TABLE A

		0.254mm (10 micron) Granules
5	density of dried granules	0.59 g/ml
	percent vesiculation ¹	65%
	weight solids	21.5%
	volume solids	36%
10	maximum granule size ²	0.012 mm (12 microns)
	median granule size	5.2x10 ⁻³ mm (5.2 microns)
	minimum granule size	3x10 ⁻³ mm (3 microns)
	vesicle size ³	5x10 ⁻⁴ -3x10 ⁻³ mm (0.5-3.0 microns)
	surface pores on granules	<(2x10 ⁻⁴ mm) (<0.2 micron)
	thickness of granule wall	1x10 ⁻⁴ - 5x10 ⁻⁴ mm (0.1-0.5 micron)

Note:

1: vesiculation determined by mercury porisimetry

2: granule size determined by Laser Diffraction Granulometer

3: internal diameters measured using scanning electron microscopy

20

EXAMPLE 3

This example illustrates the preparation of 0.01 mm (10 microns) pigmented vesiculated polyester resin granules in which the alkyl acryloyl derivative is in the first and second emulsion stages. For the purposes of this example the alkyl acryloyl derivative was chosen to be MAPTAC. The formulation has been selected as an example for use in paper applications.

		GROUP	MATERIAL	PARTS (W/W)
30		A	water	3.163
			dispersant	0.243
			antifoam	0.014
35		B	titanium dioxide pigment	9.472
		C	MAPTAC	0.243
		D	water	4.369
		E	water	1.323
40		F	polyester	7.774
			styrene	4.312
			magnesium oxide	0.043
45		G	hydroxyethyl cellulose	7.719
			poly(vinyl alcohol)	4.482
			MAPTAC	1.008
			water	29.315
50		H	water	26.318
		I	ferrous sulphate	0.003
			diethylene triamine	0.042
		J	cumene hydroperoxide	0.082
		K	bactericide	0.075
				100.000

55 The materials used and method of preparation follows that for Example 1.

The following series of experiments employ the following terms:

Freeness of pulp is a measure of the drainage rate of water through the pulp and is measured in accordance with the TAPPI (Technical Association of the Pulp and Paper Industry) Standard T227 om-75

and is also referred to as Canadian Standard Freeness.

Opacity of the paper sheet is expressed as a light scattering co-efficient (L.S.C.) and measured in accordance with TAPPI Standard T 425 om-81 using light with a wavelength of 572 nanometers.

The term handsheet is used to refer to a paper sheet made in accordance with and employing the equipment described in the TAPPI standard T205 om-81.

Conditioning refers to the conditioning atmospheres of 23.0 °C plus or minus 1 °C, and 50.0 +/- 2.0 percent relative humidity that the paper sheets are exposed to in accordance with TAPPI standard T405 om-83.

Handsheets were prepared by the following general procedure.

The furnish or solids in the pulp slurry comprised 100 percent by weight of a fully bleached chemical hardwood/softwood blend. The pulp was a commercially produced kraft pulp, and was subsequently beaten to a Canadian Standard Freeness of 415 mls. After beating, individual samples of pulp were disintegrated, stirred, and varied amounts of the pigmented vesiculated granules added.

The furnish was subsequently passed through a sheetmaker and the resultant handsheet pressed and conditioned.

EXAMPLE 4

The hereinabove general procedure for the preparation of furnishes was carried out to prepare furnish comprising a fully bleached chemical hardwood/softwood blend kraft pulp and a filler comprising pigmented vesiculated polymeric granules (PVC) as described in this invention, or comprising standard manufacture vesiculated polymeric granules (SPVG). The filler composition was an emulsion form of the pigmented vesiculated granules as described in Example 1 for the MAPTAC - PVG granules, or Example 2 for the TMAEMC - PVG granules.

The results are shown in Table B.

TABLE B

EXAMPLE 4					
RUN	SAMPLE	% ADDED*	% RETAINED OF ADDED	L.S.C.	
1.	Pulp + MAPTAC - PVG	22.0	35.1	648	
2.	"	27.5	37.5	681	
3.	"	33.0	30.1	686	
4.	"	38.5	34.0	751	
5.	"	44.0	31.5	774	
6.	Pulp + TMAEMC - PVG	3.6	73.3	589	
7.	"	6.0	84.8	630	
8.	Pulp + SPVG	32.3	3.0	497	
9.	Pulp only	-	-	434	

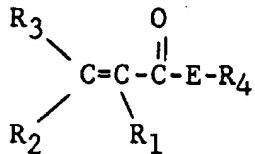
* weight solids of granules on weight solids of pulp

Example 4, Table B shows that the pigmented vesiculated polyester resin granules in which the alkyl acryloyl derivative is MAPTAC demonstrates greatly improved retention and higher opacity than the standard manufacture pigmented vesiculated polyester resin granules. If the run number 3 and run number 8 are compared, it can be seen that the granule comprising the MAPTAC has been retained at a level of 30.1% whereas the standard granule has been retained at only 3.0%. This improved retention is reflected in higher opacities. Run number 3, the granule comprising MAPTAC, has an opacity of 686; whereas run number 8, the standard manufacture granule, has an opacity of 497.

Example 4, Table B also shows that the pigmented vesiculated polyester resin granules in which the alkyl acryloyl derivative is TMAEMC demonstrates greatly improved retention and higher opacity than the standard manufacture pigmented vesiculated polyester resin granules. Run number 6 uses a granule comprising TMAEMC added at a level of 3.6% on pulp (weight solids on weight solids). The opacity obtained for this run is 589. This can be compared to run 8 which uses standard manufacture granules at an addition level of 32.2%, the opacity obtained is 497. These two runs clearly show that a higher opacity was obtained, using less weight of granules added, by the use of granules comprising TMAEMC.

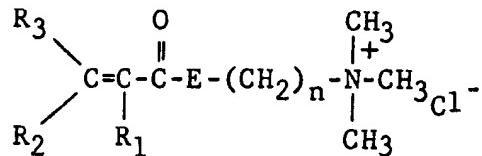
Claims

1. Vesiculated granules of cross-linked carboxylated polyester resin prepared by the free radical polymerization of a dispersion comprising (a) a substantially water-insoluble ethylenically unsaturated monomer; (b) a carboxylated unsaturated polyester resin having an acid value of from 5 to 50 mg KOH/g; (c) water; (d) a base; and (e) up to 30 weight per cent, of the non-volatile portion of both the polyester resin and the acryloyl derivative, of an alkyl acryloyl derivative of the general formula:



wherein R_1 , R_2 and R_3 are selected from H and CH_3 ; E is NH or O; R_4 is C_{1-6} alkyl substituted with Z; wherein Z is NR_5R_6 ; wherein R_5 is C_{1-4} alkyl and R_6 is H; or R_5 and R_6 are independently C_{1-3} alkyl; and quaternary C_{1-3} alkyl salts thereof.

2. Vesiculated granules according to claim 1, wherein the alkyl acryloyl derivative is a compound of the general formula:



wherein R_1 , R_2 and R_3 are selected from H and CH_3 ; E is NH or O; and n is 1 to 3.

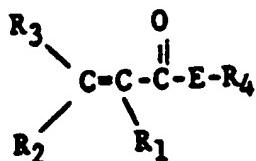
3. Vesiculated granules according to claim 1 or 2, wherein the granules contain a particulate material.
4. Vesiculated granules according to claim 3, wherein the granules contain up to 60% by volume of the particulate.
5. Vesiculated granules according to claim 3 or 4, wherein the particulate material is a pigment.
6. Vesiculated granules according to any of claims 1 to 5, wherein the unsaturated polyester resin has an acid value of from 15 to 20 mg KOH/g.
7. Vesiculated granules according to any of claims 1 to 6, wherein the alkyl acrylaryl derivative concentration is not more than 15% by weight of the unsaturated polyester resin.
8. An aqueous composition comprising vesiculated granules as claimed in any of claims 1 to 7.
9. An aqueous composition comprising vesiculated granules as claimed in any of claims 1 to 7 and a fibrous cellulosic or non-fibrous cellulosic material in the form of a paper pulp.
10. Paper containing dispersed therein vesiculated polymer granules as claimed in any of claims 1 to 7.

Patentansprüche

- 55 1. Bläschengranulat aus vernetztem carboxyliertem Polyesterharz, hergestellt durch Freiradikalpolymerisation einer Dispersion, die folgende Komponenten umfaßt:
 a) ein praktisch wasserunlösliches ethylenisch ungesättigtes Monomer,
 b) ein carboxyliertes ungesättigtes Polyesterharz mit einer Säurezahl von 5 bis 50 mg KOH/g,

- c) Wasser,
 - d) eine Base und
 - e) bis 30 Gew.-%, bezogen auf den nichtflüchtigen Anteil sowohl des Polyesterharzes als auch des Acryloylderivats, eines Alkylacryloylderivats der allgemeinen Formel:

5

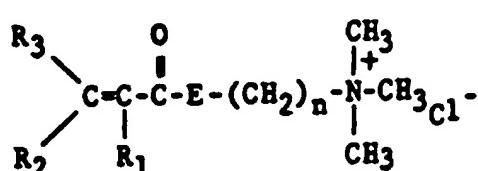


10

15 worin R_1 , R_2 und R_3 ausgewählt sind unter H und CH_3 , E NH oder O und R_4 ein durch Z substituiertes C_{1-6} -Alkyl bedeuten, wobei Z für NR_5R_6 steht, worin R_5 für ein C_{1-4} -Alkyl und R_6 für H oder R_5 und R_6 unabhängig voneinander für ein C_{1-2} -Alkyl stehen, und der quartären C_{1-2} -Alkylsalze davon.

2. Bläschengranulat nach Anspruch 1, worin das Alkylacryloylderivat eine Verbindung der allgemeinen Formel:

20



80

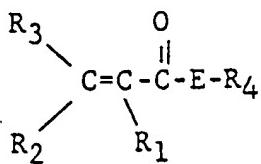
ist, worin R₁, R₂ und R₃ ausgewählt sind aus H und CH₃, E NH oder O und n eine Zahl von 1 bis 3 bedeuten.

3. Bläschengranulat nach einem der Ansprüche 1 oder 2, worin das Granulat einen in Teilchenform vorliegenden Stoff enthält.
 4. Bläschengranulat nach Anspruch 3, worin das Granulat bis zu 60 Vol.-% des in Teilchenform vorliegenden Stoffes enthält.
 5. Bläschengranulat nach einem der Ansprüche 3 oder 4, worin der in Teilchenform vorliegende Stoff ein Pigment ist.
 6. Bläschengranulat nach einem der Ansprüche 1 bis 5, worin das ungesättigte Polyesterharz eine Säurezahl von 15 bis 20 mg KOH/g besitzt.
 7. Bläschengranulat nach einem der Ansprüche 1 bis 6, worin die Konzentration des Alkylacrylarylderivats höchstens 15 Gew.-% des ungesättigten Polyesterharzes ausmacht.
 8. Wäßriges Gemisch, das ein Bläschengranulat nach einem der Ansprüche 1 bis 7 enthält.
 9. Wäßriges Gemisch, das ein Bläschengranulat nach einem der Ansprüche 1 bis 7 und ein faserförmiges oder nichtfaserförmiges Cellulosematerial in Form einer Papiermasse enthält.
 10. Papier, das ein darin dispergiertes Bläschengranulat nach einem der Ansprüche 1 bis 7 enthält.

55 Revendications

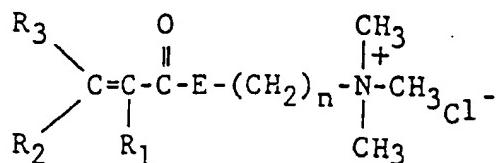
1. Granules vésiculeux de résine polyester carboxylée réticulée préparés par polymérisation radicalaire d'une dispersion comprenant (a) un monomère éthyéniquement insaturé sensiblement insoluble dans

l'eau ; (b) une résine polyester insaturée carboxylée ayant un indice d'acide de 5 à 50 mg de KOH/g ; (c) de l'eau ; (d) une base ; et (e) jusqu'à 30 pour cent en poids, par rapport à la portion non volatile totale de la résine polyester et du dérivé acrylique, d'un dérivé alkyl-acrylique de formule générale :



où R_1 , R_2 et R_3 sont choisis parmi H et CH_3 ; E est NH ou O ; R_4 est un groupe alkyle en $C_1\text{-}C_6$ substitué par Z ; Z est NR_5R_6 ; R_5 est un groupe alkyle en $C_1\text{-}C_4$ et R_6 est H ; ou bien R_5 et R_6 sont chacun indépendamment un groupe alkyle en $C_1\text{-}C_3$; ou d'un de ses sels quaternaires à groupes alkyle en $C_1\text{-}C_3$.

2. Granules vésiculeux selon la revendication 1, dans lesquels le dérivé alkyl-acrylique est un composé de formule générale :



où R_1 , R_2 et R_3 sont choisis parmi H et CH_3 ; E est NH ou O ; et n est de 1 à 3.

3. Granules vésiculeux selon la revendication 1 ou 2, dans lesquels les granules contiennent une matière particulaire.
4. Granules vésiculeux selon la revendication 3, dans lesquels les granules contiennent jusqu'à 60 % en volume de la matière particulaire.
5. Granules vésiculeux selon la revendication 3 ou 4, dans lesquels la matière particulaire est un pigment.
6. Granules vésiculeux selon l'une quelconque des revendications 1 à 5, dans lesquels la résine polyester insaturée a un indice d'acide de 15 à 20 mg de KOH/g.
7. Granules vésiculeux selon l'une quelconque des revendications 1 à 6, dans lesquels la concentration du dérivé alkyl-acrylique n'est pas supérieure à 15 % en poids de la résine polyester insaturée.
8. Composition aqueuse comprenant des granules vésiculeux tels que revendiqués dans l'une quelconque des revendications 1 à 7.
9. Composition aqueuse comprenant des granules vésiculeux tels que revendiqués dans l'une quelconque des revendications 1 à 7 et une matière cellulosique fibreuse ou cellulosique non fibreuse sous la forme d'une pâte à papier.
10. Papier contenant à l'état dispersé des granules vésiculeux de polymère tels que revendiqués dans l'une quelconque des revendications 1 à 7.